

The University of Chicago

SYNTHESES OF POLYENES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1941

By
WALTER NUDENBERG

CHICAGO, ILLINOIS

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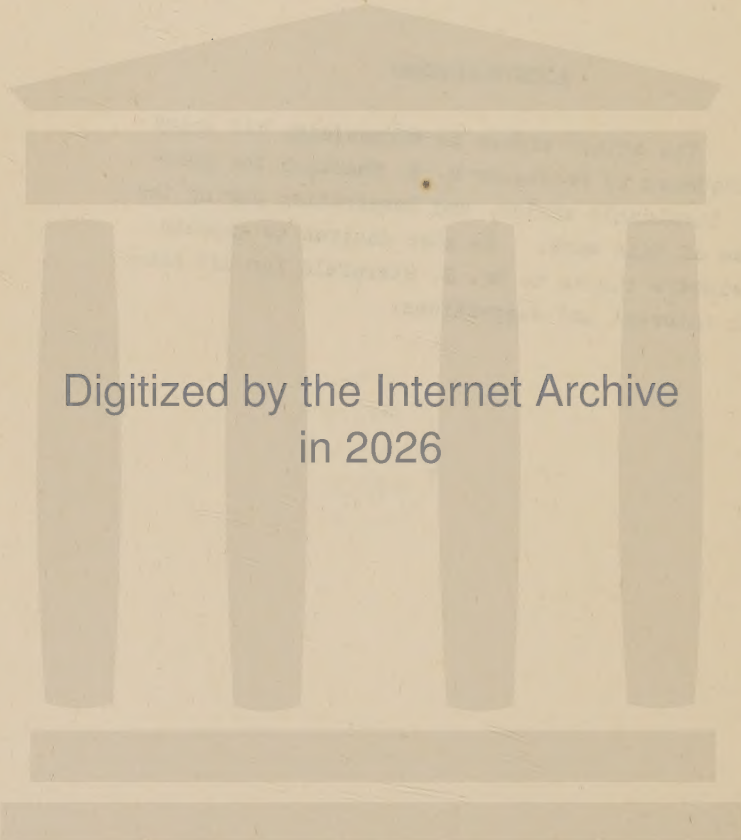
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ACKNOWLEDGMENT

The author wishes to acknowledge his great indebtedness to Professor M. S. Kharasch for guidance, invaluable advice, and inspiration during the course of this work. He also desires to express his sincere thanks to Dr. E. Sternfeld for his constant interest and suggestions.



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INTRODUCTION

The action of sodium amide¹ in liquid ammonia or other solvents on organic halides has been the subject of numerous investigations.² Table 1 is a summary of some of the organic halides which have been investigated to date.

Until 1937 it was assumed, and corroborated by experiment, that organic halides react with sodium amide to form an amine or amines (primary, secondary, and tertiary) and/or unsaturated hydrocarbons in which the number of carbon atoms is the same as in the starting product.

Shreve and Burtsfield,³ for example, have reported that the following reactions take place when n-amyl bromide reacts with sodium amide in liquid ammonia at -50°.

¹Reviews on the chemistry of the alkali amides by F. W. Bergstrom and W. C. Fernelius appear in Chem. Rev., 12, 43-179 (1933) and 20, 413, 481 (1937).

²References to some of these investigations are:

- a. Shreve and Burtsfield, Ind. Eng. Chem., 33, 218 (1941).
- b. Chablay, Chem. Zentr. 1913, I, 1003; Compt. rend., 156, 327-30 (1913).
- c. Alexieff, J. Russ. Phys. Soc., 34, 526-29 (1902); Bull. soc. chim. (3), 30, 689-90 (1903).
- d. Picon, Bull. soc. chim. (4), 35, 980 (1924).
- e. Amagat, Compt. rend., 190, 1055 (1930); Bull. soc. chim., 49, 1410 (1931).
- f. Bergstrom and Horning, Chem. Rev., 20, 432 (1937).
- g. Lespieau and Bourguel, Organic Syntheses, VI, 26, Wiley and Sons, New York (1936).
- h. Bourguel, Ann. chim. (10), 3, 341-42 (1925).
- i. Davis and Marvel, Jour. Amer. Chem. Soc., 53, 3840-51 (1931).
- j. Vaughn, Vogt, and Nieuwland, Jour. Amer. Chem. Soc., 56, 2120 (1934).
- k. Porter and Suter, Jour. Amer. Chem. Soc., 57, 2025 (1935).
- l. Coleman, Holst, and Maxwell, Jour. Amer. Chem. Soc., 58, 2310-12 (1936).
- m. Sachs, Ber., 39, 3013 (1906).
- n. Bergstrom and Fernelius, Chem. Rev., 12, 99 (1933).
- o. Bergstrom, Wright, Chandler, Gilkey, J. Org. Chem., 1, 170-78 (1936).
- p. Bergstrom and Fernelius, Chem. Rev., 20, 435 (1937).

³Shreve and Burtsfield, Ind. Eng. Chem., 33, 218 (1941).

TABLE 1

REACTIONS OF ORGANIC HALIDES WITH NaNH_2

Type of Org. Hal.	Cpds. Treated with NaNH_2	Solvent & Conditions	Substances Formed and Yield	Notes	Reference (See 2, p)
Paraffinic mono-halide	n-butyl bromide	Liq. NH_3 at -50°	19% butene, 59.1% butylamine, 10.9% dibutylamine		a
	n-hexyl bromide	Liq. NH_3 at -50°	10% hexene, 74% n-hexylamine		a
	isoamyl bromide	Liq. NH_3 at -50°	21.6% amylene, 60.2% isoamylamine, 9.4% diisoamyl amine		a
	sec-amyl bromide (2-bromopentane)	Liq. NH_3 at -50°	63.2% olefine, no amine		a
	MeI	Liq. NH_3 at -33°	MeNH_2		m
	isobutyl chloride	Liq. NH_3 at -33°	83.6% isobutylene		m
	amyl iodide	Sealed tube at 152°	mixture of three amylamines, tertiary predominates		c
	ethyl chloride	Liq. NH_3 in autoclav, 0°	30% ethyl amine, diethyl & triethyl amine		c
	$\begin{pmatrix} \text{H} \\ \text{C}-\text{CH}_2\text{Br} \\ \text{R} \end{pmatrix}$ $\begin{pmatrix} \text{R}=\text{CH}_3, \text{C}_2\text{H}_5, \\ (\text{CH}_3)_2\text{CH} \end{pmatrix}$	boiling xylene for 5-6 hours	$\begin{pmatrix} \text{H} & \text{H} \\ & \text{C}=\text{CR} \end{pmatrix}$ + small amount of $\begin{pmatrix} \text{R} & \text{H} \\ & \text{C}=\text{CH} \end{pmatrix}$		
	$\begin{pmatrix} \text{H} & \text{H} & \text{H} \\ & \text{C}-\text{C}-\text{C}-\text{Br} \\ \text{H} & \text{H} & \text{H} \end{pmatrix}$	boiling diphenyl methane	mixture of secondary and tertiary amines		
		KNH_2 in liq. NH_3 at 0° .	65%		

TABLE 1 - Continued

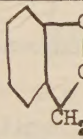
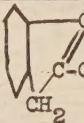
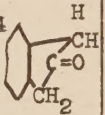
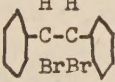
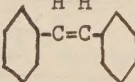
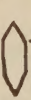
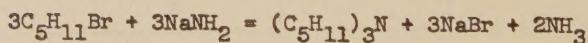
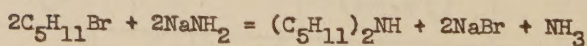
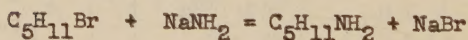
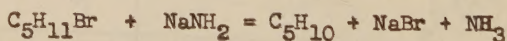
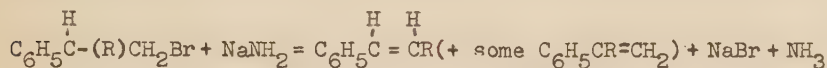
Type of Org. Hal.	Cpds. Treated with NaNH_2	Solvent & Conditions	Substances Formed and Yield	Notes	References (See n.2, p.1)
Unsaturated mono-halides		160-165° 3 mole NaNH_2 in min. oil ²	66% 		g
	C1 $\text{C}_3\text{H}_7\text{C}=\text{CHC}_2\text{H}_5$	pseudocumene at 140°	$\text{C}_3\text{H}_7\text{C}=\text{CC}_2\text{H}_5$, 40%; $\text{CH}_3(\text{CH}_2)_4\text{C}=\text{CH}$, 15%		h
	C1 $\text{C}_3\text{H}_7\text{C}=\text{CHC}_2\text{H}_5$	pseudocumene at 170°	$\text{CH}_3(\text{CH}_2)_4\text{C}=\text{CH}$, 65%		h
	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{ClH} \\ \quad \quad \\ \text{CH}_3\text{C} - \text{C} - \text{C} = \text{CH} \\ \quad \\ \text{H} \quad \text{C}_2\text{H}_5 \end{array}$	mineral oil	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{C} = \text{CH} \\ \\ \text{C}_2\text{H}_5 \end{array}$		i
	2-bromo-octene-1	Liq. NH_3 at -33° ³	hexylacetylene, 73%		j
	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{CBr} \end{array}$ 	Liq. NH_3 at -33° ³	 -C≡CH 75%		j
		Liq. NH_3	 $\xrightarrow{\text{H}_2\text{SO}_4}$ 		k
	$\begin{array}{c} \text{CH}_3 \quad \text{H} \quad \text{Br} \\ \quad \quad \\ \text{C} = \text{CH} \end{array}$ 	KNH_2 in liq. NH_3	$\begin{array}{c} \text{CH}_3 \quad \quad \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{C} = \text{C} \end{array}$ 90%		l
	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} - \text{C} - \text{C} \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$ 	Liq. NH_3 at -33° ³	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \end{array}$ 	86%	j

TABLE 1 - Continued

Type of Org.Hal.	Cpds. Treated with NaNH_2	Solvent & Conditions	Substances Formed and Yield	Notes	References (See n.2, p.1)
Aro-matics	 -Br	No solvent Heated at b.p. of bromobenzene	 -NH ₂	poor yield	m
	 F	Liq. NH ₃ KNH ₂ at room temp.	 NH ₂	good yield	n
	3 moles KNH ₂ to 1  -Cl. Halide added to NH ₃	KNH ₂ in liq. NH ₃ at -33°	 -NH ₂ 52% () ₂ -NH 15.5% () ₃ -N  NH ₂		o
	 -C-Cl H	KNH ₂ in liq. NH ₃ at -33°	1)  -C=C-  or 2) compound (C ₇ H ₆) ₄ m.p. 144° Conditions under which 1 or 2 is formed are not stated.		p

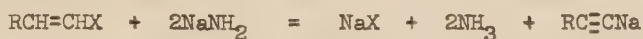


These same authors have shown that amination takes place with paraffin monohalides containing primary halogen atoms. Amine formation is decreased with branched chain alkyl halides. Furthermore, the increase in length of the carbon chain increases the yields of the primary amines. Shreve and Rothenberger⁴ have found that the use of solvents other than liquid ammonia, namely, ligroin, ether, and benzene, leads to the formation of little or no amine. Mlle. Amagat⁵ has found that unsaturated hydrocarbons are formed when phenylalkylethyl bromides are heated with sodium amide in boiling xylene for 5 to 6 hours, in accordance with the general equation:



The yield of expected hydrocarbon, $\text{C}_6\text{H}_5\overset{\text{R}}{\underset{|}{\text{C}}}=\overset{\text{H}}{\underset{|}{\text{C}}}\text{H}$, is very small. The major product of the reaction is a 1-phenyl-2-alkylethene, a substance formed by rearrangement during the elimination of the hydrogen bromide. 1-Bromo-3-phenyl propane, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, is not attacked by sodium amide in boiling xylene, but in boiling diphenyl methane it is converted to a mixture of the corresponding secondary and tertiary amine.

Unsaturated monohalides are converted to acetylenic hydrocarbons by treatment with sodium amide in an inert liquid or in liquid ammonia.⁶



X = Cl or Br; R = alkyl or hydroaromatic radical.

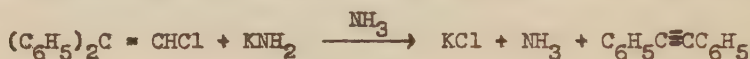
Unsaturated monohalides of the type $\text{RCCl}=\text{CH-R}'$ (R' = aliphatic) are usually converted to acetylenic hydrocarbons of the type

⁴Shreve and Rothenberger, Ind. Eng. Chem., **29**, 1360 (1937).

⁵Amagat, Compt. rend., **190**, 1055 (1930); Bull. soc. chim., **49**, 1410 (1931).

⁶Bourguel, Ann. chim. (10), **3**, 341-42 (1925); Bourguel, Bull. soc. chim. (4), **41**, 1478 (1927); Lespieau, Bull. soc. chim. (4), **37**, 421 (1925); Meunier and Desparmet, Bull. soc. chim. (4), **1**, 342-46 (1907); Meunier and Desparmet, Compt. rend., **144**, 273-75 (1907); Vaughn, Vogt, and Nieuwland, Jour. Amer. Chem. Soc., **56**, 2120-22 (1934).

$R^mC\equiv CH$ when the reaction is carried out at 150° in an inert liquid.⁷ Vaughn, Vogt, and Nieuwland⁸ report that ethyl amyl acetylene did not undergo any change upon treatment with sodium amide in liquid ammonia for 16 hours. This indicates that a high temperature is necessary for the rearrangement to the acetylene containing a terminal triple bond. Coleman, Maxwell, and Holst⁹ treated chloro and bromoethenes of the type $RC\equiv CH$, ($R = \text{aryl}$) with potassium amide, dissolved in liquid ammonia. Hydrogen halide is readily removed and a rearrangement to a tolane takes place.



An o, m, or p-substituted phenyl in the chloro or bromoethene appears in the same configuration in the product. For instance, 1,1 di-o-tolylbromoethene and potassium amide give di-o-tolyl acetylene. These reactions are interpreted on the same basis as other rearrangements involving the removal of HX from an organic halide, namely, the removal of the halide ion from the diaryl chloro or bromoethene leaving a carbon atom with a sextet of electrons. A pair of electrons is attracted from the neighboring carbon atom; the aryl group with its pair of electrons shifts to the adjacent carbon atom. The tolane is then formed by intramolecular electron rearrangement and loss of a proton.

Chloroform and bromoform react with sodium amide (in the absence of a solvent) to form sodium halide and sodium cyanide.¹⁰



Carbon tetrachloride¹¹ when treated with potassium amide in liquid ammonia reacts to give a quantitative yield of potassium chloride and large quantities of gas consisting of six parts nitrogen to one part hydrogen. The solution, originally clear, becomes opal-

⁷Bourguel, Ann. chim. (10), 3, 341-42 (1925); ibid., 199-285, 325-85.

⁸Vaughn, Vogt, and Nieuwland, Jour. Amer. Chem. Soc., 56, 2120 (1934).

⁹Coleman, Maxwell, and Holst, Jour. Amer. Chem. Soc., 58, 2310-12 (1936).

¹⁰Meunier and Desparmet, Bull. soc. chim. (4), 1, 342-46 (1907).

¹¹Kraus, Chem. Rev., 26, 100 (1940).

escent and gradually turns brown; finally free carbon is precipitated in an amount equal to one-half that originally due to carbon tetrachloride. Details of this reaction have not been worked out.

Acetylenic hydrocarbons result from the action of sodium amide on 1,1, 2,2- or 1,2-paraffin dihalides under an inert hydrocarbon of high boiling point (toluene, xylene, paraffin oil) or in liquid ammonia at -33° .



Sometimes ethylenic hydrocarbons are formed in reactions a and b.¹²

Hexachloroethane¹³ and hexafluoroethane¹⁴ have been treated with sodium amide. Hexachloroethane is decomposed by sodium amide to form a mixture of products which include sodium cyanide, chloride, and cyanamide. Hexafluoroethane reacts violently with sodamide at 250° , but no products have been isolated.

Small yields of aniline were obtained by Sachs¹⁵ by heating chloro or bromobenzene with sodium amide. Chlorobenzene reacts with sodium amide at 110° - 120° in the presence of copper gauze or copper powder, to give triphenylamine, while under similar conditions tribenzyl amine is obtained from benzyl chloride and triisoamyl amine from isoamyl chloride.¹⁶ Mixed tertiary amines may be made in this fashion. Chloro, bromo, iodo benzenes react very rapidly with a liquid ammonia solution of potassium amide at -33° to give aniline and diphenylamine with smaller quantities of triphenyl amine and p-amino biphenyl, in proportions

¹²Bourguel, Compt. rend., 177, 688 (1923); Ann. chim.(10), 3, 196, 198-202, 211, 213-18, 225-28, 335, 339; Meunier and Desparmet, Bull. soc. chim(4), 35, 481-84 (1924); Lespieau, Bull. soc. chim.(4), 29, 528-35 (1921); Bourguel, Ann. chim.(10), 3, 225-29, 343-50 (1925); Vaughn, Vogt, and Nieuwland, J. Amer. Chem. Soc., 56, 2120 (1934).

¹³Titherly, J. Chem. Soc., 71, 460-61 (1897).

¹⁴Swarts, Bull. soc. chim., Belg., 42, 114-18 (1933); C. A., 27, 5052 (1933).

¹⁵Sachs, Ber., 39, 3013 (1916).

¹⁶Matter, German patents: 301, 450; 361, 832; Chem. Abst., 13, 324 (1919); Chem. Zent., 1918, I, 43, 149.

which depend upon experimental conditions.¹⁷ In boiling ether or benzene the above reactions do not occur. α -Bromonaphthalene, o- and p-chlorobiphenyl, o-chloroaniline and o-dichlorobenzene likewise react readily with a liquid ammonia solution of potassium amide, but the reactions are very complicated. α -Fluoronaphthalene is more slowly converted by an excess of potassium amide in liquid ammonia solution to α -naphthylamine in fairly good yield. Fluorobenzene is not completely decomposed by potassium amide in the same time as other aromatic halides.¹⁸

A survey of the literature indicates that, in general, when organic halides are treated with bases halogen acids are eliminated and ethylene derivatives are formed. In certain cases, however, two molecules of the halide condense to form an unsaturated dimer. It has been reported that a solution of potassium amide in liquid ammonia converts benzyl chloride either to stilbene or to a compound of the composition $(C_7H_6)_4$ and m.p. 144° , depending upon the conditions.¹⁹ No yield of either of the products is reported. Other substances are claimed to be formed in this reaction. 9-Fluorenyl bromide reacts with potassium hydroxide in acetone solution to yield bifluorenylidene.²⁰ Liquid ammonia reacts with 9-chlorofluorene to give besides difluorenylamine, an appreciable quantity of biphenylene ethylene and a trace of primary amine (9-fluorenylamine).²¹ Plissov²² prepared nitro substituted stilbenes from 2,4-dinitrobenzyl chloride, p-nitrobenzyl chloride, and o-nitrobenzyl chloride by the action of alcoholic potassium hydroxide at $-6^\circ C$. Bromodiphenacyl, $C_6H_5-\overset{\overset{O}{\parallel}}{C}-\underset{\underset{BrH}{\mid}}{C}-\underset{\underset{H}{\mid}}{C}-\overset{\overset{O}{\parallel}}{C}-C_6H_5$, was prepared by treat-

¹⁷Bergstrom, Wright, Chandler, and Gilkey, J. Org. Chem., 1, 170-78, 179-88 (1936).

¹⁸Bergstrom and Fernelius, Chem. Rev., 12, 110 (1933).

¹⁹Bergstrom and Fernelius, Chem. Rev., 20, 435 (1937); Rousseau and Urner, Unpublished work at Stanford U.

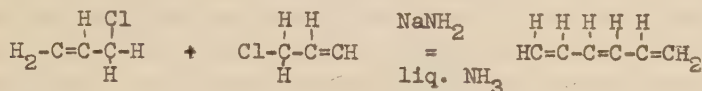
²⁰Thiele and Wahnscheidt, Ann., 376, 278 (1910).

²¹Courtot and Peticolas, Compt. rend., 180, 297 (1925).

²²Plissov, J. Chim. Ukraine, 1, 417-24 (1925); Chem. Abstracts, 20, 2851 (1926); Plizov, Ukrainskii Khim. Zhur., 4, Sci. Pt. 241-79 (1929); Chem. Abstracts, 24, 1108 (1929).

ing phenacyl bromide, $C_6H_5\overset{O}{\underset{\text{||}}{C}}-CH_2Br$, with sodium ethylate in alcohol.²³

In this laboratory sodamide in liquid ammonia has been used successfully as a condensing agent.²⁴ The equation below represents the reaction which takes place when allyl chloride is treated with sodium amide in liquid ammonia.



The formation of hexatriene supports the hypothesis that halides of weakly electronegative radicals²⁵ will condense when treated with sodium amide in liquid ammonia if there is a hydrogen atom on the carbon atom to which the halogen atom is attached. Since the electronegativity of the allyl radical would be decreased by substituents on the α -carbon and only very little affected by substituents on the β -carbon, the method here described should apply to the preparation of many substituted hexatrienes.

As a preparative method for polyenes, the sodium amide-liquid ammonia method affords many advantages over the usual methods.²⁶ The operations involved are simple and rapid. Sodium

²³Fritz, Ber., 28, 3032 (1895).

²⁴Kharasch and Sternfeld, J. Am. Chem. Soc., 61, 2318 (1939).

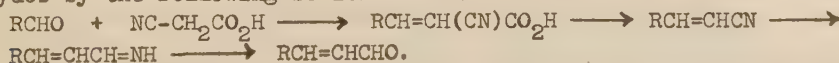
²⁵Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932); Kharasch and Swartz, J. Org. Chem., 3, 405 (1938).

²⁶a) Van Romburgh, J. Chem. Soc., 90, 130 (1906); Proc. Roy. Acad., Amsterdam, 15², 1184 (1913), prepared hexatriene by decomposition of 5-divinyl glycol diformate, or the dehydration of 1,5-hexadiene-4-ol;

b) Farmer, Laroia, Switz, and Thorpe, J. Chem. Soc., 1927, 2937-58, reduced unsaturated carbonyl compounds to pinacols, replaced hydroxyl groups by halogens, and abstracted the halogens by zinc;

c) Kuhn and Grundmann, Ber., 69B, 1754-65 (1936), made polyene dicarboxylic acids, $HO_2C-(CH=CH)_nCO_2H$, by condensing compounds of type $Me(CH=CN)_{n-1}CO_2H$, with $(CO_2Et)_2$ in presence of sodium or potassium ethylate followed by an appropriate series of reactions;

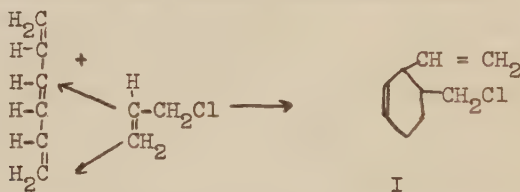
d) Wittig, Kethur, Klein, and Wilthrock, Ber., 69B, 2078-87 (1936); Chem. Abst., 30, 820, prepared unsaturated aldehydes by the following series of reactions:



Stannous chloride in ether containing HCl reduces only the nitrile group.

amide is added to a liquid ammonia solution of allyl chloride as rapidly as the violence of the reaction permits, and the products are then isolated.

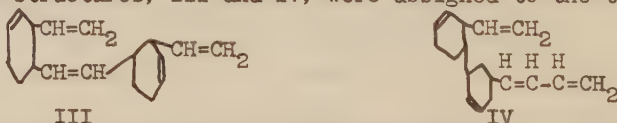
Kharasch and Sternfeld²⁷ found that the yield of hexatriene was dependent upon the order of addition. Thus when sodium amide was added to allyl chloride a 30% yield of hexatriene was obtained; whereas, when the allyl chloride was added to sodium amide only 10% of hexatriene was isolated, and a large amount of a high boiling material. The nature of the high boiling material is dependent upon experimental conditions. When three moles of allyl chloride was dissolved in liquid ammonia and two moles of sodium amide added the main product (50%) was found to be 1-chloromethyl-2-vinyl-cyclohexene-3,²⁸ formed by condensation of allyl chloride with hexatriene according to the following scheme:



When an excess of sodium amide is employed, polymers of hexatriene can be isolated, uncontaminated with halogen compounds. Thus, 1-butadienyl-2-vinyl-cyclohexene-3 was isolated in 40% yield. Dimerization had taken place by 1,4 addition of a terminal double bond of a hexatriene molecule to another hexatriene molecule.



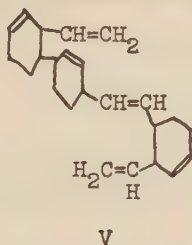
A trimer which had five double bonds was isolated, and the two probable structures, III and IV, were assigned to the trimer.



27 Kharasch and Sternfeld, J.Am.Chem.Soc., 61, 2318 (1939).

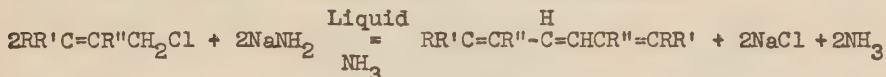
28 Alder and Windemuth, Ber., 71B, 1939 (1938), condensed cyclopentadiene and anthracene with allyl chloride at 150°-180°C., under fairly high pressures.

Since the trimer did not react with maleic anhydride, it was suggested that III is the correct structure. A tetramer of hexatriene was obtained which contained six double bonds. The tetramer did not react with maleic anhydride. It was assumed on the basis of the above evidence that its structure was best represented by V.



DISCUSSION

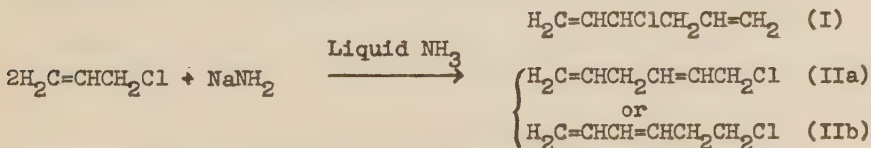
In the present work, the reaction of sodium amide with allyl chloride in liquid ammonia has been further investigated and data bearing on the generality of the reaction



have been obtained from a study of the interaction of the various halides listed in Table 2 with sodium amide in liquid ammonia.

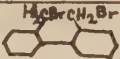
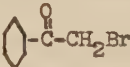
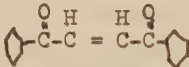
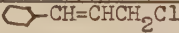
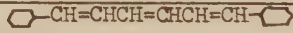
Inspection of Table 2 shows that only those compounds which have in common an unsaturated group adjacent to the $-CH_2X$ group undergo the sodium amide-liquid ammonia condensation. The activating effect which unsaturated groups exert on nearby atoms²⁹ is here manifest. The last two items (no. 11 and 12) in the table are examples of condensations between unlike molecules. Geranyl chloride (No. 7) did not give the expected product.

The probability that the conversion of allyl chloride to hexatriene proceeds through the intermediate formation of a chlorohexadiene was investigated.



²⁹Allen and Blatt, Gilman, Organic Chemistry, Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1938, chap. 6, p. 543.

TABLE 2

Reactants	Products	% Yield of Liquid NH ₃ Method	% Yield of Other Investigators
1. $\text{CH}_2=\text{CHCH}_2\text{Cl} + (0.5 \text{ mol. NaNH}_2)$ allyl chloride	chlorohexadiene	20%	
2. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl} + (1 \text{ mol. NaNH}_2)$ β -methylallyl chloride	2,5-dimethylhexatriene $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2$	27%	
3. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl} + (0.5 \text{ mol. NaNH}_2)$ methylallyl chloride	chloro-2,5-dimethylhexadiene	34%	
4.  dibromo-o,o'-bitolyl	 phenanthrene	80%	
5.  phenacyl bromide	 sym.dibenzoyl ethylene (trans m.p. 110°C.)	42%	78-83% ^a
6. $\text{BrCH}_2\text{CH}=\text{CHCH}_2\text{Br}$ 1,4-dibromo-2-butene	Linear molecule of type $\text{BrCH}_2(\text{CH}=\text{CH})_n\text{CH}_2\text{Br}$	100%	
7. $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{Cl}$ geranyl chloride	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{NH}_2$ or $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_2)_2\text{C}(\text{NH}_2)-(\text{CH}_3)\text{CH}=\text{CH}_2$ geranyl amine	35%	43% ^b
8.  cinnamyl chloride	 diphenylhexatriene	10%	18% ^c

^aLutz, *Organic Syntheses*, 20, 29 (1940), by treatment of fumaryl chloride with benzene in the presence of aluminum chloride.

^bForster and Cardwell, *J. Chem. Soc.*, 103, 1345 (1913), by treatment of geranyl chloride with sodium azide and subsequent reduction of the azide.

^cKuhn and Winterstein, *Helv. Chim. Acta*, 11, 87 (1928), from cinnamic aldehyde.

TABLE 2 - Continued

Reactants	Products	% Yield Liquid NH ₃ Method	% Yield of Other Investi- gators
9.  -CH ₂ Cl benzyl chloride	 -CH=CH-  stilbene	100%	
10. 2,3-dichloroprop- ene-1 $\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$	Resinous material	...	
11. benzyl chloride + β-methylallyl chloride	 -CH=CHC(CH ₃)=CH ₂ phenyl isoprene	23%	
	 -CH=CH-  stilbene	13%	
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ 2,5-dimethylhexatriene	35%	
	mixture of polymers and stilbene	29%	
12. benzyl chloride + allyl chloride	 -CH=CHCH=CH ₂ phenylbutadiene	14%	
	 -CH=CH-  stilbene		
	$\text{CH}_2=\text{CHCH}=\text{CHCH}=\text{CH}_2$ hexatriene	86%	
	polymers		

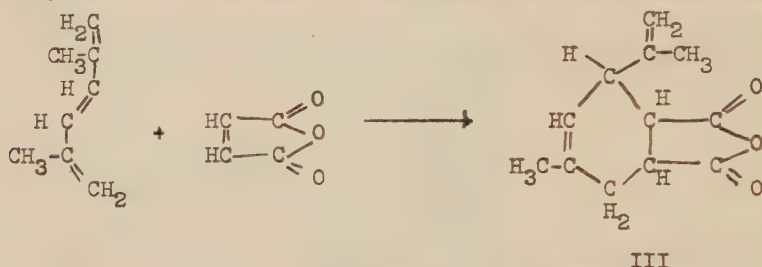
Two molecular equivalents of allyl chloride were treated with one of sodamide and the lower-boiling reaction product carefully fractionated. A 20% yield of a pure chlorohexadiene, b.p. 46-47.5° (96 mm.), n_D^{20} 1.4483, was obtained. Levene and Haller³⁰ have reported the preparation of 3-chloro-1,5-hexadiene (I) by treatment of allylvinylcarbinol, but recorded no physical constants other than the rotations of the optically active forms. Further treatment of the purified chlorohexadiene with sodamide yielded butadienyl-2-vinylcyclohexene-3³¹ instead of monomeric hexatriene.

³⁰Levene and Haller, J. Biol. Chem., **83**, 185 (1929).

³¹Kharasch and Sternfeld, J. Am. Chem. Soc., **61**, 2318 (1939).

The interaction of equimolecular quantities of β -methylallyl chloride and sodamide in liquid ammonia led to the formation of 2,5-dimethylhexatriene in yields comparable to those of hexatriene obtained from allyl chloride.³² The product was identified by hydrogenation to 2,5-dimethylhexane, and by condensation with maleic anhydride to form 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride (III).

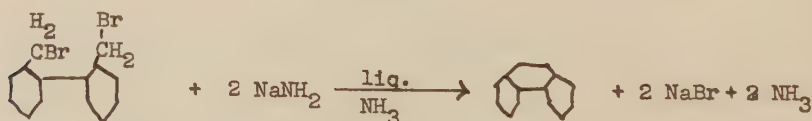
The physical constants of 2,5-dimethylhexatriene observed in this Laboratory do not agree with those previously reported by Bourguet and Rambaud,³³ who believed they had prepared this compound by treating the glycol, 2,5-dimethyl-2,5-dihydroxy-3-hexene,



with dilute hydrochloric acid at 95° for eight days, but who recorded no proofs of the structure or homogeneity of their product.

Treatment of two moles of β -methylallyl chloride with approximately one mole of sodium amide in liquid ammonia yielded an intermediate chloro-2,5-dimethylhexadiene, b.p. 33-34° (5 mm.), 160° (752 mm.); n_D^{20} 1.4612. Further treatment of this chloride with sodium amide gave 2,5-dimethylhexatriene.

That sodium amide in liquid ammonia may be used for ring closure is indicated by the formation of phenanthrene from ω, ω' -dihalo-o,o'-bitolyl.



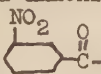
ω, ω' -dibromo-o,o'-bitolyl is easily prepared by the bromination

³²Kharasch and Sternfeld, *J. Am. Chem. Soc.*, **61**, 2318 (1939).

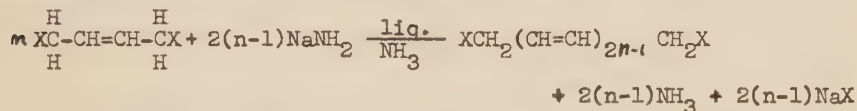
³³Bourguet and Rambaud, *Bull. soc. chim.* (4) **47**, 173 (1930); Johnson and Johnson, *J. Am. Chem. Soc.*, **62**, 2615 (1940).

of o,o'-bitolyl;³⁴ in the reaction cited it gives an 80% yield of phenanthrene. Other compounds similar to this dibromobitolyl are more difficult to synthesize. The usefulness of the reaction given is limited by the same factors which limit the preparation of substituted diacylethylenes. These limitations are described in the next paragraph.

By the preparation of symmetrical dibenzoyl ethylene, it has been shown that the sodamide condensation may be extended to halides $R-CH_2X$ in which R is an acyl group. This method cannot, however, be employed with compounds containing certain reactive groups. Nitro groups, for example, are reduced by sodamide in liquid ammonia.³⁵ An attempt to condense m-nitrophenacyl chloride,

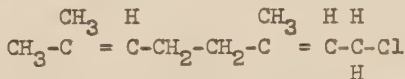
 $-C(=O)CH_2Cl$, resulted in the formation of a dark viscous liquid, from which no pure compound could be isolated. Furthermore, compounds like chloroacetone react more rapidly with liquid ammonia than they do with the sodamide. In such cases the products obtained by the method in question contain nitrogen.

A dihalide of the type, $XCH_2-CR=CR'-CH_2X$, when treated with sodamide in liquid ammonia would be expected to condense with itself at both ends to give a linear compound of large molecular weight. The reaction should be as follows:



Such a compound of high molecular weight was obtained from 1,4-dibromo-2-butene, $BrCH_2-\overset{H}{\underset{H}{C}}=C-CH_2Br$. Its molecular weight (calculated from its bromine content of 11.3%) is 1416. It should accordingly consist of 24 butene molecules linked together, and should contain 47 conjugated double bonds.

Assuming the generally accepted structure (I)

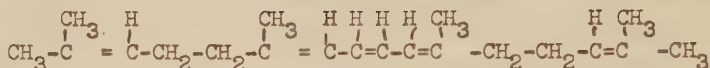


I

³⁴Kenner and Turner, *J. Chem. Soc.*, 99, 2108 (1911).

³⁵Bergstrom and Buehler, *Chem. Rev.*, 20, 461 (1937), found that nitrobenzene reacts with sodium amide in liquid ammonia at -33°C., in the presence of β -naphthol to give phenylazo- β -naphthol, $\phi N=NC_{10}H_6OH\beta$.

for geranyl chloride, it was thought that the tetramethylhexadecapentaene (II)



II

might be formed when this chloride was treated with sodamide in liquid ammonia; however, the major product isolated was an amine, the hydrochloride of which contained 7.34% N, in agreement with the formula, $\text{C}_{10}\text{H}_{20}\text{NCl}$. This formula is that of geranyl amine hydrochloride, or an isomer thereof. Forster and Cardwell³⁶ prepared geranyl amine (b.p. 105° at 19 mm.) by treating geranyl chloride with sodium azide and then reducing the azide with zinc and acetic acid. They reported that their hydrochloride melted at 120° . The geranyl amine hydrochloride prepared in the course of the present work melted at $142-144^\circ$. Although geranyl chloride is usually regarded as a chloride of the type $\text{RC}=\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\overset{\text{H}}{\underset{|}{\text{C}}}-\text{Cl}$,

it has not been demonstrated that the material consists entirely of the primary chloride. From the work of Kharasch, Kritchevsky, and Mayo,³⁷ it seems probable that such samples consist of a mixture of primary and secondary chlorides. The secondary chloride,

$\text{RC}-\overset{\text{H}}{\underset{|}{\text{C}}}-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2$, when treated with sodamide might be expected to give an amine and/or the hydrocarbons,



The primary chloride can react with allylic rearrangement to yield the secondary amine.

Cinnamyl chloride, when treated with sodamide in liquid ammonia, gives 10% of diphenyl hexatriene.



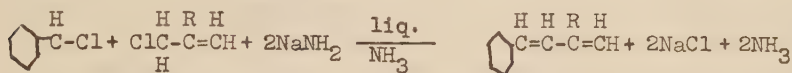
The nature of the other products formed depends upon the quantity of sodamide used. When the usual 10% excess of sodamide was em-

³⁶Forster and Cardwell, *J. Chem. Soc.*, 103, 1343 (1913).

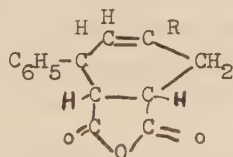
³⁷Kharasch, Kritchevsky, and Mayo, *J. Org. Chem.*, 2, 489 (1937).

ployed the produce was a resin containing chlorine. This resin may have been formed by the condensation of diphenyl hexatriene with cinnamyl chloride just as chloromethylvinylcyclohexene is formed by the condensation of hexatriene with allyl chloride.³⁸ The product could not be isolated in pure form. When a large excess of sodamide (7 moles per mole of cinnamyl chloride) was used the product was a polymerized hydrocarbon containing three diphenyl-hexatriene units per molecule.

The usefulness of the sodamide reaction in the preparation of unsymmetrical olefins has been demonstrated by the preparation of 1-phenyl-3-methylbutadiene from benzyl chloride and β -methylallylchloride, as well as by the formation of 1-phenylbutadiene from benzyl chloride and allyl chloride.



The other expected products (stilbene and 2,5-dimethyl hexatriene in the first case, and stilbene and hexatriene in the second case) were also formed. Both of the phenylbutadienes reacted with maleic anhydride to give addition products of type



Mechanism of the sodamide condensation.--In the course of the present work on the synthesis of polyenes, a number of condensing agents besides sodamide were examined. Solvents other than liquid ammonia were also tried. Benzyl chloride was used as the test halide, since its condensation product, stilbene, is easily isolated. The results are summarized in Table 3. So far as these results show, sodamide is the only effective condensing reagent, and liquid ammonia the only solvent suitable for the reaction in question.

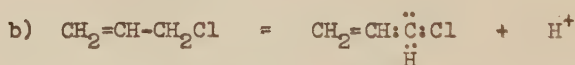
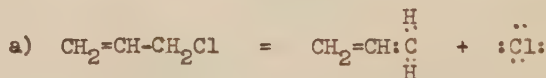
All the halides here employed are of the type $\text{R-CH}_2\text{X}$, and in each case R is highly electronegative. Consequently both the halogen atom and the hydrogen atom or atoms on the carbon atom

³⁸Kharasch and Sternfeld, J. Am. Chem. Soc., **61**, 2318(1939).

TABLE 3

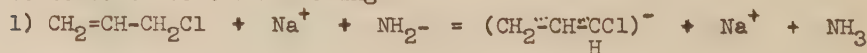
Condensing Agent	Solvent	Product	Yield
KOH (powdered).. NaOC ₂ H ₅ Na formamide.... Na formamide.... NaNH ₂ NaNH ₂ NaNH ₂	Liquid ammonia Liquid ammonia Liquid ammonia Formamide Ether Ligroin Liquid ammonia	Benzylamine hydrochloride Benzylamine hydrochloride Benzylamine hydrochloride Dibenzyl formamide Benzylamine hydrochloride Benzyl chloride recovered Stilbene	5% 5% 5% 55% 15% .. 100%

carrying the halogen are far more labile than the corresponding atoms in compounds like ethyl chloride or vinyl chloride. Allyl chloride, for example, can dissociate in either of the two following ways:

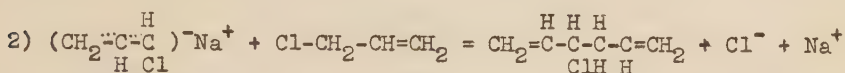


Equation (a) represents the manner in which the chlorine atom may be replaced as negative groups such as hydroxyl, alkoxyl, or amino simultaneously approach the organic halide. Equation (b) shows a less common form of dissociation of organic halides. To obtain an appreciable amount of hydrogen ion by the dissociation of allyl chloride a very strong base must be employed. Sodamide is such a base.

On these grounds the following mechanism for the reaction of sodamide with allyl chloride is suggested. The first step is believed to be the following:

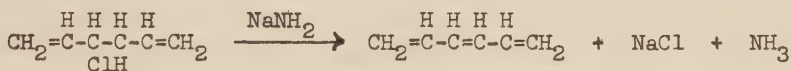


The reaction, a simple ionic neutralization, analogous to the neutralization of a weak acid with a strong base, is extremely rapid, even though sodamide is not very soluble in liquid ammonia. Whenever an excess of sodamide is present in the solution containing the organic halide a deep color ranging from red to purple develops. This color is probably due to the allyl chloride ion. The allyl chloride ion then reacts with allyl chloride to replace the chlorine atom, giving chlorohexadiene and chloride ion as in equation 2.



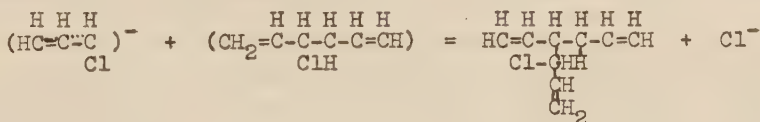
V

Compound V has been isolated under the conditions stated (page 13). When treated with another mole of NaNH_2 it reacts as follows:



The chlorine atom (in eq. 2) is replaced by an allyl chloride residue, just as the halogen atom is replaced by an alkoxyl group in a Williamson synthesis.

It might be predicted that in some cases V, rather than lose a molecule of hydrogen chloride, would react with IV.



IV

V

VI

VI might again react with IV or V and reactions of this type might continue until a large molecule had been formed. The only statement which can be made about such series of reactions is that under the experimental conditions here described IV is formed in high concentration and would be expected to react with another molecule of IV rather than with a molecule of V. However, some high boiling material is always found in the end product of a polyene synthesis.

The above discussion shows one reason why sodamide alone brings about the polyene condensation. The other condensing agents investigated are bases which are not strong enough to form

the metal salts of the organic halides. Such weaker bases may however be employed to condense stronger acids. Potassium hydroxide in acetone, for example, reacts on 9-bromofluorene to form difluorenylidene,³⁹ and liquid ammonia alone reacts with 9-chlorofluorene to give difluorenylidene.⁴⁰ Sodamide acts only in liquid ammonia probably because it is soluble only in that medium; in organic solvents such as ether and benzene it is extremely insoluble.

EXPERIMENTAL PART

2,5-Dimethylhexatriene.--The method used was essentially that described by Kharasch and Sternfeld.⁴¹ One hundred thirty-five grams (1.5 mole) of redistilled ρ -methylallyl chloride was added dropwise to one liter of liquid ammonia in a 2-liter unsilvered Dewar flask. Sixty-eight grams (1.7 mole) of sodamide was added intermittently during the addition of the methylallyl chloride. A vigorous reaction ensued after each addition of sodamide. The reaction mixture was stirred for one hour after addition of all the sodamide, then transferred from the Dewar flask to a 2-liter round-bottomed flask. The Dewar flask was rinsed with low-boiling ligroin, and the washings were added to the flask.

The ammonia was evaporated and distilled water and ligroin added to the residue. The layers were shaken and separated. The organic layer was washed with water, and dried over anhydrous sodium sulfate. The ligroin was then removed by distillation through a column containing a tantalum spiral. Distillation of the residue was carried out at 110 mm. on an oil-bath with the use of the tantalum column. A few milliliters distilled at 30-73° (111 mm.) and 22 g. (27%) was collected at 73-75° (110-111 mm.). A portion of material, b.p. 73-75° (110-111 mm.), was redistilled through a Podbielniak column. A constant-boiling fraction, b. p. 90.2° (200 mm.), n_D^{21} 1.5150, was taken for analysis.

³⁹Thiele and Wahnschiedt, Ann., **376**, 278 (1910).

⁴⁰Courtot and Peticolas, Compt. rend., **180**, 297 (1925).

⁴¹Kharasch and Sternfeld, J.Am.Chem.Soc., **61**, 2318 (1939).

Anal. Calcd. for C_8H_{12} : C, 88.82; H, 11.18. Found: C, 88.88; H, 11.45.

2,5-Dimethylhexatriene boiled at 145° at 747 mm. The melting point was -9° . Heating of the compound near its boiling point for any length of time caused it to become colored and raised its boiling point, indicating rapid polymerization.

The dimethylhexatriene, dissolved in methyl alcohol, underwent smooth hydrogenation in the presence of platinum oxide to yield 2,5-dimethylhexane, b.p. $107.5-108.5^\circ$ (745 mm.), n_D^{21} 1.3925. Gardner and Joseph⁴² report b.p. $107-108.5^\circ$ (755 mm.), n_D^{21} 1.3922 for this compound. Egloff⁴³ gives b.p. 109.3° (9760 mm.), n_D^{20} 1.39295.

Hydrogenation.--0.0938 gram of dimethylhexatriene, b.p. 58° (51 mm.), in methyl alcohol solution absorbed 53.6 ml. of hydrogen (cor.) (calcd. for C_8H_{12} and 3 double bonds, 58.4 ml. of hydrogen).

By heating of equivalent amounts of 2,5-dimethylhexatriene and maleic anhydride in dry benzene in a sealed tube at 80° for seven hours, 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride (III) was obtained. After three crystallizations from ligroin (b.p. $70-80^\circ$) the white crystalline product melted at $115-116^\circ$.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut. equiv., 103. Found: C, 69.85; H, 7.17; neut. equiv., 107.

Distillation was carried out in some runs at 51 mm., at which pressure 2,5-dimethylhexatriene distilled at 58° to give a product of n_D^{20} 1.5122, d_4^{20} 0.7822. The product obtained at this lower temperature and pressure did not polymerize as readily as that obtained at higher pressures. It had the same melting and boiling points at atmospheric pressure.

Preparation of Chloro-2,5-dimethylhexadiene.--Twenty-six grams (0.88 mole) of sodamide, was added over a period of one hour to a solution of 93 g. (1 mole) of β -methylallyl chloride in liquid ammonia. After the usual treatment the following fractions were obtained: 11 g. b.p. $57-67^\circ$ (50-51 mm.) (2,5-dimethyl-

⁴²Gardner and Joseph, J. Am. Chem. Soc., **61**, 2551 (1939).

⁴³G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, N. Y., 1939, p. 53.

hexatriene and chloro compounds); 25 g. b.p. 34-36° (6 mm.) of chloro-2,5-dimethylhexadiene and some higher-boiling material which tended to polymerize on distillation at 6 mm.

The chlorodimethylhexadiene was redistilled, boiling at 33-34° (5 mm.); n_D^{20} 1.4612. Its boiling point at 752 mm. is 16

Anal. Calcd. for $C_8H_{13}Cl$: C, 66.42; H, 9.06; Cl, 24.51. Found: C, 66.12; H, 9.38; Cl, 24.13.

When the chlorodimethylhexadiene was distilled at higher pressures the chlorine analyses were low and the carbon and hydrogen high. The compound tends to lose hydrogen chloride at higher temperatures.

Treatment of the chlorodimethylhexadiene with sodamide in liquid ammonia yielded a liquid, b.p. 58-60° (51 mm.), which, when heated with maleic anhydride in dry benzene, gave the addition product already obtained from 2,5-dimethylhexatriene, m.p. 115-116°. The melting point of a mixture with the known anhydride showed no depression.

Preparation of Chlorohexadiene.--To a solution of 78 g. (1 mole) of allyl chloride in 800 ml. of liquid ammonia was added 24.5 g. (0.5 mole) of sodamide. The mixture was worked up in the usual manner. Upon distillation 12 g. of chlorohexadiene came over at 46-47.5° at 96 mm., n_D^{20} 1.4483. It boiled at 115° at 748 mm. with slight decomposition.

Anal. Calcd. for C_6H_9Cl : C, 61.80; H, 7.72; Cl, 30.4. Found: C, 62.35; H, 7.94; Cl, 30.02.

The compound tends to lose hydrogen chloride even at room temperature. On treatment with excess sodamide in liquid ammonia it gave the dimer of hexatriene, b.p. 85-87° (9 mm.), n_D^{20} 1.513

Of the remaining material from the reaction 15 g. (30%) was chloromethylvinylcyclohexene,⁴⁴ b.p. 45-50° (9 mm.), n_D^{20} 1.4672.

Absorption Spectra.--Ultraviolet and infrared absorption studies on dimethylhexatriene and the maleic anhydride addition product of hexatriene and dimethylhexatriene were very generously made by Drs. Bradley, Richardson, and Liddel of American Cyanamid Company. To quote from their communication:

⁴⁴Kharasch and Sternfeld, J. Am. Chem. Soc., **61**, 2318 (1939).

The ultraviolet absorption curve for 2,5-dimethylhexatriene is characterized by three intense narrow absorption bands at 3680, 3830, and 3980 mm^{-1} . We associate these bands with the presence of three conjugated carbon to carbon double bonds in a chain-type aliphatic compound because of their similarity to the corresponding bands found at 3550, 3700, and 3850 mm^{-1} in the spectrum of α -eleostearic acid. The 130 mm^{-1} shift toward higher wave numbers (shorter wave lengths) of these bands for the 2,5-dimethylhexatriene is the result of the lower molecular weight of this compound. When the extinction coefficients are compared on a molecular basis the intensity of absorption per molecule is found to be but slightly greater for the α -eleostearic acid as indicated in Table 4.

TABLE 4

Band	2,5-Dimethylhexatriene			α -Eleostearic Acid		
	Wave Number	Extinction Coefficient*		Wave Number	Extinction Coefficient*	
		Specific	Molecular		Specific	Molecular
I	3680	338.8	36,800	3550	131.8	36,900
II	3830	421.7	45,600	3700	163.0	47,100
III	3980	311.9	33,660	3850	128.8	36,050

*The specific extinction coefficient (K) represents the absorption per unit weight of the compound while the molecular extinction coefficient (E_m) represents the absorption per molecule.

$$K = d/Lc \quad E_m = KM = d/Lc_m$$

where d is the optical density $\log I_0/I$, L is the length in centimeters of the absorption cell filled with solution of concentration c in grams per liter or c_m in moles per liter.

The infrared spectrum of this compound (dimethylhexatriene) in the region 1000-2000 cm^{-1} shows those bands which have been observed in similar compounds. The band at 1780 cm^{-1} is the overtone of the 900 cm^{-1} C=C band. The infrared absorption due to the conjugated double bond system appears at 1615 cm^{-1} . Since this is the only triply conjugated system we have observed, we cannot say how these differ from double conjugation, if in any manner. The methyl bands appear at 1455 and 1372 cm^{-1} . The terminal $=\text{CH}_2$ band appears at 1435 cm^{-1} . Two other weak bands appear at 1319 cm^{-1} and 1255 cm^{-1} .

The spectroscopic data for the maleic anhydride addition products of hexatriene and 2,5-dimethylhexatriene shows very lit-

tle evidence for conjugated carbon to carbon double bonds. Accordingly, the structures are those of vinyl and isopropenyl, rather than ethylidene and isopropylidene, tetrahydrophthalic anhydrides, in contradiction to the work of Farmer and Warren.⁴⁵

Diphenylhexatriene.--Cinnamyl chloride (15 gr.) in 100 cc. dry ether and sodamide (3.4 g.) were added in alternate small lots to 400 cc. liquid ammonia. After the addition the mixture was stirred for 15 minutes; the ammonia was then evaporated. The organic residue was taken up in ether, the ether solution washed with water, dried over anhydrous sodium sulfate, and the ether evaporated. When the remaining liquid was cooled, 2 g. of diphenylhexatriene separated. This material was collected on a filter and the remaining liquid distilled. Cinnamyl chloride (1.5 g.) was collected at 85-95° at 2 mm. pressure. The temperature then rose rapidly; and 1 g. diphenylhexatriene distilled at 175-185° at 2 mm. pressure. It solidified in the condenser, m.p. 197-199°. The residue in the flask showed no tendency to distill and turned quite dark during the distillation of hexatriene. When it cooled, it set to a hard resin from which no crystals could be obtained. This residue still contained halogen.

Sodamide (18 g.) in liquid ammonia was treated with a solution of cinnamyl chloride (15 g.) in ether. After the usual treatment, 10 g. of a yellow solid was obtained: this substance softened at 150-160° and melted at 165°. It could not be crystallized from any solvent. It contained no halogen. Mol. wt. (micro Rast).

Calc. for $(C_{18}H_{16})_3$: 696; Found: 697.

The low yields of the diphenylhexatriene of m.p. 199° may be explained by the formation of other stereoisomers of this compound; six different forms are possible. Kuhn and Winterstein⁴⁶ prepared diphenylhexatriene from cinnamic aldehyde. Their overall yield was 18%.

Dibenzoyl ethylene.--Phenacyl bromide (10 g.) in 40 cc. dry ether and sodamide (3 g.) were added in alternate small lots to 300 cc. liquid ammonia. After evaporation of the ammonia, ether and water were added to the reaction mixture. The ether

⁴⁵Farmer and Warren, J. Chem. Soc., 897 (1929).

⁴⁶Kuhn and Winterstein, Helv. Chim. Acta, 11, 87 (1928).

solution was washed with water and dried over anhydrous sodium sulfate, then the ether was evaporated in vacuo. Yellow crystals of dibenzoyl ethylene (2.5 g.) were obtained. This material, after one crystallization from ethyl alcohol melted at 111° . The residue was a syrup, containing nitrogen; it was not further investigated. A method for preparing dibenzoyl ethylene (yield 78-83%) has been described by Lutz.⁴⁷ Bromodiphenacyl, $\text{C}_6\text{H}_5\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\text{CHBr}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{C}_6\text{H}_5$, has been obtained by Fritz⁴⁸ from phenacyl bromide and sodium ethylate in ethyl alcohol. The yield is not given in his paper and the details of the preparation are meagre.

Phenanthrene.--Dibromoditolyl (2 g., m.p. $86-87^{\circ}$) in 30 cc. dry ether was added to a suspension of sodamide made from 1.2 g. sodium in 100 cc. liquid ammonia. After the ammonia had evaporated, ether and water were added. The ether solution was washed, dried, and the ether was evaporated, there was left as a residue 950 mg. phenanthrene (m.p. $97-100^{\circ}$).

"Polymer" from 1,4-dibromobutane-2.--Twenty-four g. 1,4-dibromobutene-2,⁴⁹ m.p. 53° , in 75 cc. benzene were added to 14.5 g. NaNH_2 in 500 cc. liquid ammonia. The mixture was stirred for three hours; then the ammonia was evaporated, and a solution of 11 g. ammonium bromide in 200 cc. water was added. The flocculent precipitate was collected on a filter, washed thoroughly with water, and dried. Yield, 6 g. of a fine brown powder which does not melt below 350° .

Anal. Calcd. for $\text{C}_{96}\text{H}_{98}\text{Br}_2$: C, 81.4; H, 7.0; Br, 11.6. Found: C, 82.17; H, 6.43; Br, 11.10.

Geranylamine.--Geranyl chloride (64 g. or 0.37 mole, b.p. $75-81^{\circ}$ at 3-4 mm.) in 300 cc. of ether and sodamide (22 g. or 0.55 mole) were added in alternate small portions to 1500 cc. of liquid ammonia. The reaction mixture was then stirred for four hours. The material was worked up in the usual manner, with ether as the solvent. The ether was removed from the dried ether solution and the residue was distilled in vacuo. The following fractions were collected: I. $27-62^{\circ}$ at 1 mm., small forerun;

⁴⁷Lutz, Organic Synthesis, 20, 29 (1940).

⁴⁸Fritz, Ber., 28, 3032 (1895).

⁴⁹Thiele, Ann., 368, 340 (1899).

II. 62-65° at 1 mm., 20 g. (35% yield of geranylamine); III. higher boiling residue containing halogen. Crystals were deposited from III after it had cooled. I. contained a mixture of hydrocarbons (not identified) and geranylamine. II. was geranylamine. III. was a mixture of geranylamine and geranyl chloride which when heated gave geranylamine hydrochloride and a hydrocarbon. When a portion of the geranylamine was treated in ligroin with hydrogen chloride, a white precipitate of geranyl amine hydrochloride was obtained, m.p. 142-144°.

Anal. Calcd. for $C_{10}H_{20}NCl$: N, 7.38. Found: N, 7.54.

1-Phenyl-3-methylbutadiene.--A mixture of benzyl chloride (63 g., 0.5 mole), b-methylallyl chloride (49 g., 0.54 mole), and sodamide (43 g., 1.1 mole) were added in alternate small lots over a period of about 45 minutes to 1500 cc. of liquid ammonia. The reaction mixture was then stirred for three hours. The liquid ammonia was evaporated, and the residue taken up in a mixture of low boiling ligroin and ether. The ether ligroin solution was washed four times with water and then dried over anhydrous sodium sulfate. The ether and ligroin were removed from the dried solution by distillation on a water bath. After removal of the solvents, stilbene crystallized out. This stilbene was collected on a Buchner funnel and washed with low boiling ligroin. All operations were carried out as rapidly as possible. A yield of 6 g. (13%) was thus obtained. After the ligroin had been removed from the filtrate from the stilbene, the residue was distilled in vacuo into a receiver cooled with CO_2 -acetone mixture. The following fractions were obtained: I. 25-67° at 2 mm., 11.3 g. containing a small amount of solvent, 2,5-dimethylhexatriene and phenylmethylbutadiene; II. 67-70° at 2 mm., or 105-108° at 12 mm., 16.8 g. or 23.3% of 1-phenyl-3-methylbutadiene which crystallized in the receiver; III. above 70° at 1 mm., 38 g. of material which crystallized on cooling; this material was a mixture of stilbene, 1-phenyl-3-methylbutadiene and dimethylhexatriene polymer. In the literature the following data are given for 1-phenyl-3-methylbutadiene, m.p. 27°, b.p. 115° at 18 mm.;⁵⁰ b.p. 124° at 32 mm.,⁵¹

⁵⁰V. Grignard, Ann. Chim. (7), 24, 486 (1901).

⁵¹A. Klages, Ber., 35, 2651 (1902).

m.p. 37° , b.p. 105° at 12 mm.;⁵² m.p. 28° , b.p. 117° at 16 mm.⁵³

By heating equivalent amounts of 1-phenyl-3-methylbutadiene and maleic anhydride in dry benzene in a sealed tube at 100° for 6 hours, 4-methyl-6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was obtained. After two recrystallizations from ligroin (b.p. $107-118^{\circ}$) the white product melted at $90-91^{\circ}$.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%. Found: C, 74.56%; H, 6.14%.

4-methyl-6-phenyl-1,2,3,6-tetrahydrophthalic acid, m.p. 194° with decomposition, was obtained by heating a small portion of the corresponding anhydride in boiling water for one-half hour.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21%; H, 6.20%. Found: C, 69.42%; H, 6.73%.

The 1-phenyl-3-methylbutadiene, dissolved in methyl alcohol, underwent hydrogenation in the presence of platinum oxide, to yield isoamyl benzene, b.p. 193° at 744 mm., n_D^{20} 1.4831. Ipatieff and Schmerling⁵⁴ report isoamyl benzene b.p. $197-199^{\circ}$ at 760 mm. (corr.), n_D^{20} 1.4835.

1-Phenylbutadiene.--The procedure used here was the same as that used with benzyl chloride and methylallyl chloride. Benzyl chloride (63 g., 0.5 mole), allyl chloride (40 g., 0.52 mole), and sodamide (44 g., 1.1 mole) were used in 1500 cc. of liquid ammonia.

The ether and ligroin were removed from the reaction mixture by distillation at reduced pressure. The receiver was cooled with CO_2 -acetone. Crystals, probably hexatriene, separated from the cooled ether-ligroin distillate. After all the solvent was removed, 9 g. of material was collected at $63-65^{\circ}$ under 2-3 mm. pressure. This fraction was phenylbutadiene (14% of theoretical) which, when redistilled, came over at $75-77^{\circ}$ under 6 mm. pressure. When the heating was continued, the residue suddenly polymerized with the evolution of much heat and with a marked darkening of the material. Heating was discontinued at this point. The material remaining in the distilling flask solidified on cooling; it probably consisted of a mixture of stilbene with polymerized butadiene.

⁵²Kohler and Heritage, Amer. Chem. Jour., **43**, 486 (1910).

⁵³Auwers and Eisenlohr, J. prakt. Chem. (2), **84**, 46(1911).

⁵⁴Ipatieff and Schmerling, J. Am. Chem. Soc., **60**, 1476 (1938).

By heating equivalent amounts of 1-phenylbutadiene and maleic anhydride (as described for 1-phenyl-3-methylbutadiene) 6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was obtained. After three crystallizations from ligroin, b.p. 107-118°, the product melted at 119-120°.

When 6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was heated with boiling water for 30 minutes the corresponding acid was obtained, m.p. on rapid heating, 200-203° (with decomposition).

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.26%; H, 5.73%. Found: C, 68.33%; H, 6.02%.

2,5-Dichlorohexatriene.--This compound is apparently very unstable. An attempt was made to prepare it by treating 2,3-dichloropropene-1 with sodamide in liquid ammonia. A great deal of resinous material was formed, but only a small amount of a dark colored liquid. This liquid, when distilled in vacuo, polymerized with explosive violence.

SUMMARY

1. Reactions of some organic halides with sodium amide in various solvents are reviewed.

2. The condensation of allyl chloride is described.

3. The condensations of β -methylallyl chloride, 2,3-dichloropropene-1, cinnamyl chloride, phenacyl bromide, ω,ω' -dibromo, o,o'-bitolyl, 1,4-dibromobutene-2, and geranyl chloride, as well as the condensation of benzyl chloride with allyl and methallyl chloride are described. Sodium amide in liquid ammonia is the condensing agent.

4. A probable intermediate in the formation of 2,5-dimethylhexatriene from sodium amide and β -methylallyl chloride, a chloro-2-5-dimethylhexadiene has been isolated. The corresponding compound from allyl chloride, a chlorohexadiene has been obtained.

5. The ultraviolet and infrared absorption spectra of dimethylhexatriene have been determined.

6. Spectroscopic data indicate that the maleic anhydride addition product of hexatriene is 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride rather than the 3-ethylidene anhydride as postulated by Farmer and Warren. The corresponding compound from 2,5-dimethylhexatriene is 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride.

7. A mechanism for the reaction is suggested.

